Int. J. Corros. Scale Inhib., 2014, **3**, no. 3, 151–159

Phosphonic acid derivatives used in self assembled layers against metal corrosion

T. Abohalkuma,[1,2] F. Shawish[2] and J. Telegdi[3,4]

[1]*PhD School of Materials Sciences and Technologies;Óbuda University / Bécsi út 96/B, 1016 Budapest, Hungary*
[2]*Libyan Petroleum Institute, Girgarisg Road Km7, Tripoli, Libya*
[3]*Institute of Media Technology and Light Industry; Óbuda University/ Doberdó út 6., 1034 Budapest, Hungary*
[4]*Department of Functional and Structural Materials, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, 1117 Budapest, Magyar tudósok körútja 2, Hungary*
E-mail: telegdi.judit@ttk.mta.hu

Abstract

The preparation of self assembled molecular (SAM) layers needs molecules with a small hydrophilic and a big hydrophobic molecular parts. Special molecules were chosen where the head group was in all cases phosphonic group, but there were significant differences in the other molecular part. In one case a medium sized carbon chain with a single double bound, in the second case a long alkyl chain with fluoro atoms, and in the third case a polymer molecular part represented the hydrophobic molecular section. Our work was focused on the preparation and characterization of their SAM layers they formed on solid surfaces under the different conditions. The molecular films were deposited from organic solvents on different metal surfaces covered by oxide layer. In the case of the layer with double bounds, polymerization of the molecules on the surface with UV light was applied. The modified surfaces were characterized by the wettability and their anti-corrosion activity was determined in linear polarization experiments.

According to the numerical results the wettability of the surfaces differed significantly, *i.e.*, we successfully modify the solid surface with the coatings. The anti-corrosion activity of the coated surfaces depends on the molecules used for layer deposition. The samples with fluoro-alkyl chains gave the best results, not only their contact angles were very high but their anti-corrosion effectiveness was the best.

Keywords: *self assembled molecular layer, phosphonic acids, wettability, corrosion.*

Received: March 27, 2014; in revised form: May 8, 2014.

1. Introduction

Metals like carbon steel and stainless steel have found a wide use in technical and industrial applications. The surfaces of iron based alloys are covered by inhomogeneous oxides, which are not stable against external influences. Due to their instability against

corrosion, either the application of dissolved inhibitors or a protective layer, mostly an organic coating, is necessary to decrease the undesired corrosive deterioration. In spite of all developed technologies, corrosion attacks can take place due to failures at the metal/ electrolyte interface [1].

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in neutral media. The results presented in numerous publications show that most organic inhibitors act by as 2D or 3D inhibitors, *i.e.*, they can either be adsorbed on the metal surface or inhibit the corrosion via precipitation [2–5].

Organic phosphonic acids are very good materials for metal corrosion inhibition. They can easily form complexes with different metal ions [5, 6, 7]. They have been widely used as water treatment agents because of their low toxicity, high stability and corrosion inhibition activity in neutral aqueous media.

Several environmentally friendly alternative metal pre-treatment were already proposed. One of the new potential alternatives is the application of self-assembly molecular layer for forming ultrathin organic layers [8].

As a flexible method of forming thin and well-defined organic coatings such as hydroxamic acids and phosphonice acids on a variety of solid surfaces [9–13], self assembly molecular layers have attracted increased attention during the last decades. The deposition process is simple and inexpensive since the films form spontaneously upon immersion of a solid substrate into a dilute solution of organic adsorbate molecules [1].

Self-assembly requires a relatively strong bond between the substrate and an atom or moiety in the molecule, and an additional lateral interaction among molecules in the monolayer [8]. These monolayers are highly ordered molecular assemblies, formed spontaneously by physi- or chemisorptions through the molecule head group. Once adsorbed to the surface, these molecules organize themselves through van der Waals interaction among the long aliphatic chains [14].

The use of organic solvents in the deposition process has some disadvantages: (*i*) the dissociation of surface active functional group is hindered in organic solvents, and (*ii*) on an industrial scale, organic solvents are increasingly disfavored [8]. In spite of the undesired organic solvents the big advantage of their use is the high concentration of the amphiphilic molecules which helps to decrease the layer formation time.

The contact angle (CA) measurement is an important parameter for characterization of surfaces. It is a common measure of the hydrophobicity of a solid surface. It is well established that the contact angle measurements does not only gives information on the surface wettability but can be used in the calculation of solid surface energy [15].

2. Experimental

2.1 Sample preparation

Metal samples used in our experiments for the contact angle measurements were carbon steel, 304 and 316L stainless steel. These samples were prepared first by cutting to the dimensions of 10 mm in width and 11 mm in length then ground using emery papers with

the grits of 220, 800, 2200 and 4000. They were later polished with diamond paste, washed with water, degreased with acetone and dried at atmospheric conditions. For the linear polarization measurements, the carbon steel samples were cleaned with 15% HCl in an ultrasonic bath for 60 s, washed with distilled water, degreased with acetone and left to dry.

2.2 Preparation of self-assembled monolayers

Metal samples were immersed in solutions containing chemicals used for surface film preparation which were dodecyl phosphonic acid, styrene-co-styrophosphonic acid, fluorophosphonic acid and undecenyl phosphonic acid. The concentrations of each chemical were 5×10^{-2} M (5E−2M) as well as 5×10^{-3} M (5E−3M) and the immersion time ranged between 15 min, 2 h, 4 h, 24 h up to 48 h for contact angle measurements and 15 min, 30 min, 1 h, 2 h, 4 h, and 24 h for the polarization measurements. After the required contact time, the samples were taken out and the superfluous remedy of the solution was removed by dipping in the pure organic solvent. Finally the coated metal samples were left to dry on air.

2.3 Linear polarization measurements

A hand-made apparate was used for the linear polarisation measurements. The electrodes were polarized with 10 mV from the corrosion potential. The current is measured and from these data, together with the characteristics of the metal, the apparate calculated the corrosion rate.

After the formation of the SAM layers on metal samples, they were immersed in the electrolyte containing sodium chloride and sodium sulphate ions and the corrosion rate was measured at zero time and 15 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 21 h, 22 h, 23 h, 24 h, 26 h, 48 h, and 72 h.

2.4 Contact angle measurements

The characterization of the pre-coated metal surfaces was carried out with the use of the dynamic surface tensiometer (DST 9005 Nima) in order to determine the dynamic contact angle values of each sample. The test liquid was Milli Q water and the depth of immersion depth was 8 mm with a speed of 5 mm/min. The number of cycles was 5 for each sample to test the compactness of the layer.

3. Results and discussion

3.1 Results of contact angle measurements

3.1.1 Influence of the amphiphilic molecules

Figure 1 shows the results of carbon steel covered by different phosphonic acid layers formed in 24 h. As can be noticed the highest contact angle was achieved by fluorophosphonic acid layer with values of 129° and 80° (advancing and receding, respectively). This proves the formation of a compact layer on the metal surface and the

influence of the superhydrophobic fluorine atoms; both factors reduced the wettabily. Evaluating the influence of the film formation time there was an increase in the advancing contact angle values for the undecenyl phosphonic acid: after 4 h the contact angle was 83° that increased to 107° when 24 h were left for the self assembling process. The increase in the concentration of the coating solution had an impact but a small one on contact angles.

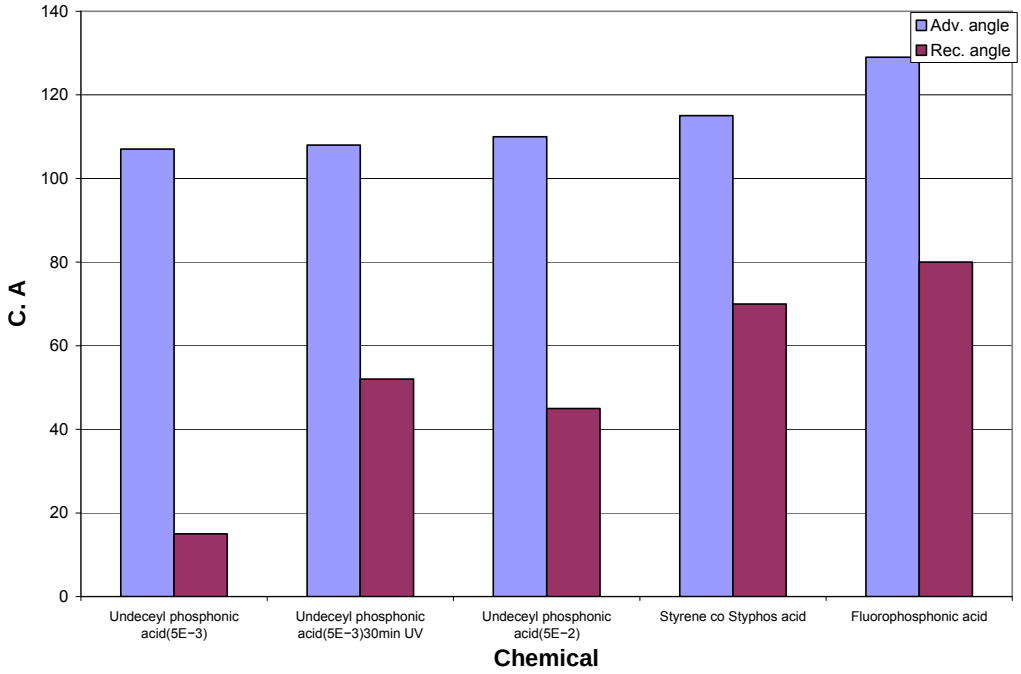

Figure 1. Contact angle values for carbon steel covered by layers of different chemicals after 24 h; influence of the concentration of coating materials as well as of layer formation time shown in the case of the undecenyl phosphonic acid after; in the cases of styrene-co-styphos acid and fluorophosphonic acid, the layer formation time was 24 h and the concentration was 5×10^{-3} M.

Results of contact angles measured on 304 stainless steel covered by nanolayers (Fig. 2) show that after 24 h deposition time the highest contact angle value was achieved with the fluorophosphonic acid (127° as an advancing angle). It was interesting that there was almost no change in the contact angle values when the coating was formed from a more concentrated solution.

The layer formation time affected the quality of the layer when the dodecyl phosphonic acid was used where the contact angle values increased from 95° measured at 15 min to 118° at 24 h which indicates that longer time was needed for the formation of a good compact layer.

The effect of layer forming chemicals such as, undecenyl phosphonic acid, styrene-co-styphos acid and fluorophosphonic acid, on 316LN stainless steel samples are illustrated in Fig. 3. It can be noticed that the highest advancing contact angle of 118° was achieved with the fluorophosphonic acid. All three metal samples after 24 h long immersion in undecenyl phsphonic acid gave the same results. Similar contact angle values were

achieved by layers formed from styrene-co-styphos acid on carbon steel and on stainless steel 304. The hydrophobicity of the stainless steel 316 coated by styrene-co-styphos layer did not reach that one measured on the other two metals.

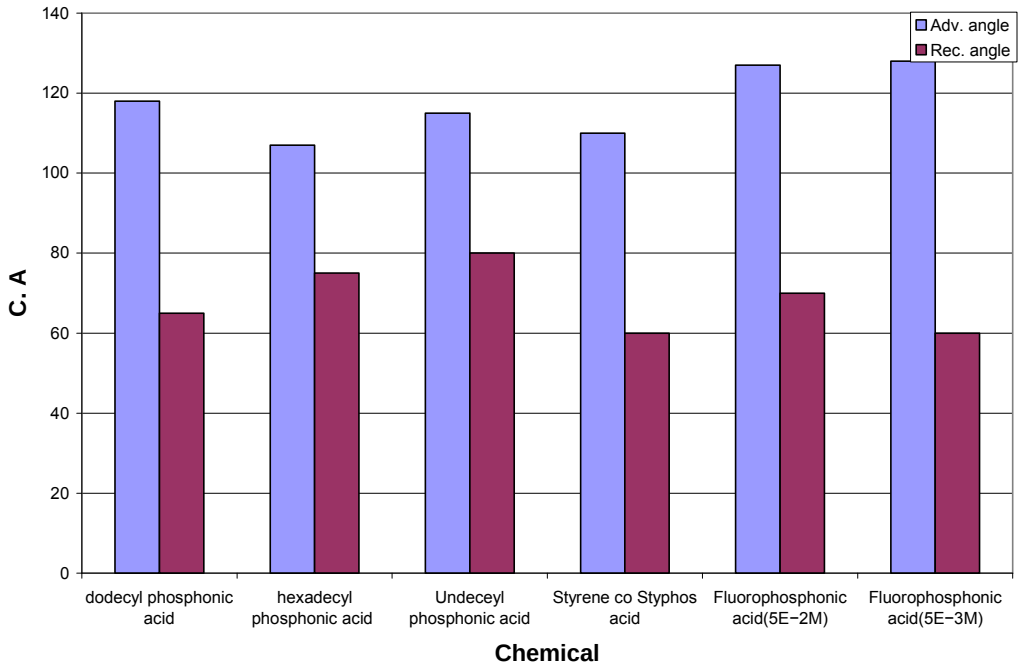

Figure 2. Contact angle values for 304 stainless steel covered by layers of different chemicals after 24 h.

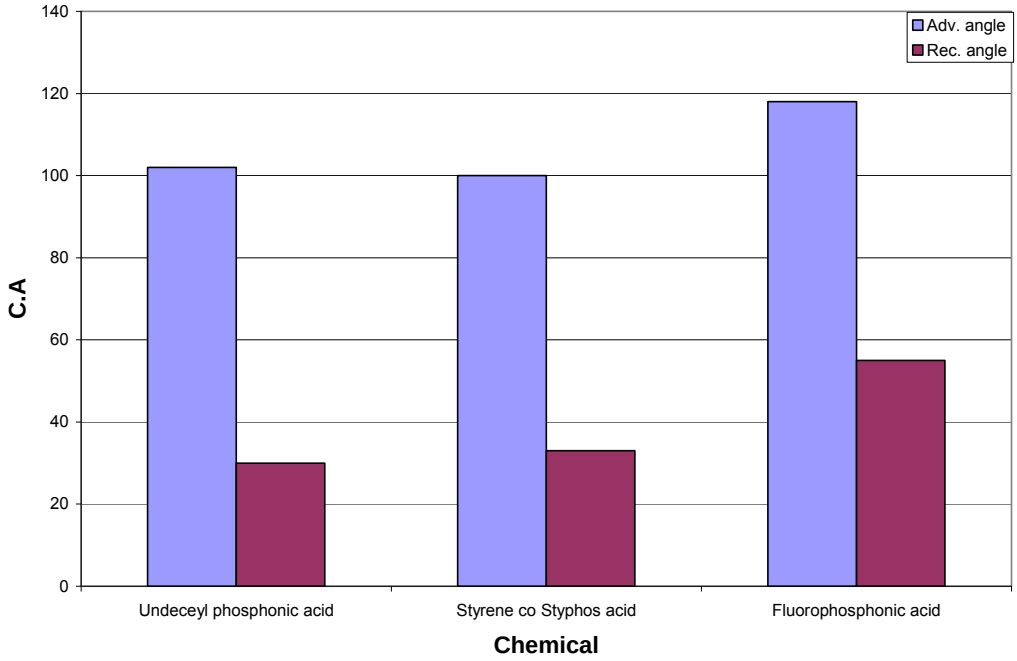

Figure 3. Contact angle values for 316LN stainless steel covered by layers of different chemicals after 24 h.

3.1.2 Influence of cycling (in measuring of the advancing an receding CA)

There was a big difference in the advancing angle when the number of cycles increased. When undecenyl phosphonic acid was used for SAM preparation in 24 h, after four dips the originally measured advancing CA (107°) changed to 60° which indicates that the layer was loose and the water could penetrate to the metal surface.

3.1.3 Curing the layer with UV light

As the contact angle values showed that the layers formed from the undecenyl phosphonic acid were not compact which was due to the double bond in the alkyl chain, we have decided to polymerize the layer through the unsaturated bonds by UV light. After exposing the metal sample coated by undecenyl phosphonic acid layer to a UV light ($\lambda = 254$ nm) for 30 min, the advancing angle values were 108° for the first dip and 105° for the other dips. This indicates that the layer became more compact for the influence of the UV light because of the polymerization of the double bounds (Table 1).

Table 1. Contact angle values for carbon steel surface pre-coated with undecenyl phosphonic acid.

Metal surface	Chemical	Layer formation time	Θ dyn Adv./ retr.	Remarks
Carbon steel	Undecenyl phosphonic acid (5E−3)	24 h	107°/15° (1st dip) 60°/15° (4 other dips)	
			108°/52° (1st dip) 105°/45° (4 other dips)	Exposed to UV for 30 min each side

3.2 Results of linear polarization measurements

Figures 4–6 show the results of the corrosion rate values for metal coupons covered by SAM layers formed by the three chemicals on carbon steel surfaces. As shown the lowest value (less than 0.15 mm/y) was achieved with the fluorophosphonic acid layers formed at 4 h and 24 h. This was due to that phosphono groups interact strongly with the metal oxides, mostly through the formation of stable M–O–P bonds. The polynuclear complexes have usually low solubility and their formation at the interface can inhibit the metal dissolution. In the case of SAM layers, the corrosion rate values were higher than 0.2 mm/y for those layers when the formation time was shorter (15 min, 30 min and 2 h). The layers formed by undecenyl phosphonic acid at 24 h gave relatively high contact angle results, but the corrosion rate value increased with time which indicates that the layer began to break and corrosion took place. Layers formed by styrene-co-styphos acid showed that these layers gave high corrosion rate at all times of formation. This was due to the

loose structure of the SAM layer and as a consequence the aggressive solution penetrated to the metal surface so corrosion took place at active metal surfaces. The big hydrophobic molecular parts in the styrene-co-styphos layer do not allow the formation of a well-ordered structure.

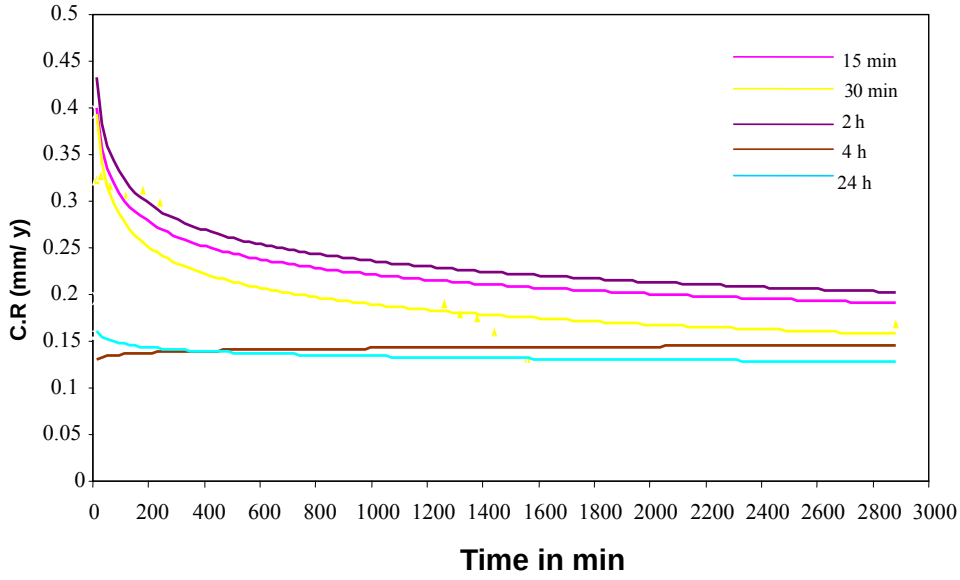

Figure 4. Corrosion rate values for layers formed by fluorophosphonic acid on carbon steel.

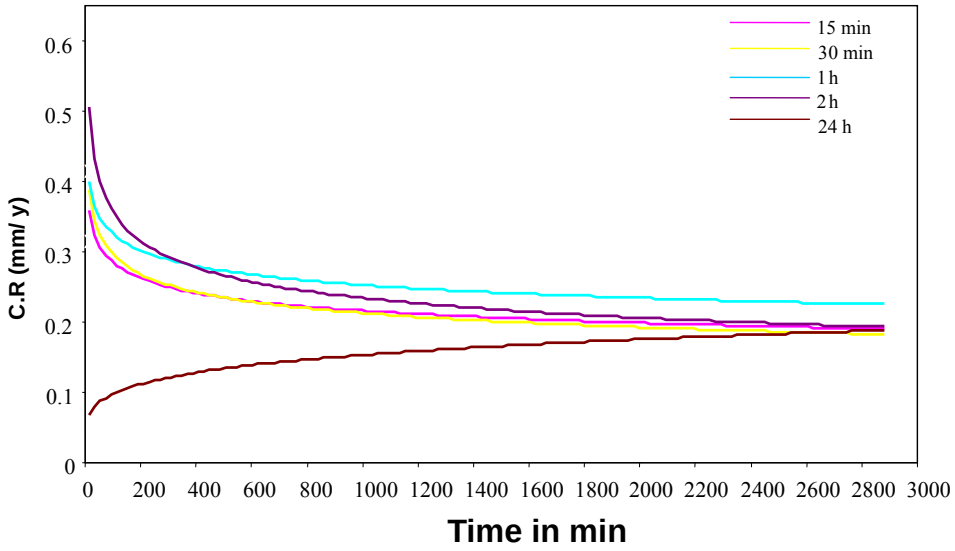

Figure 5. Corrosion rate values for layers formed by undecenyl phosphonic acid on carbon steel.

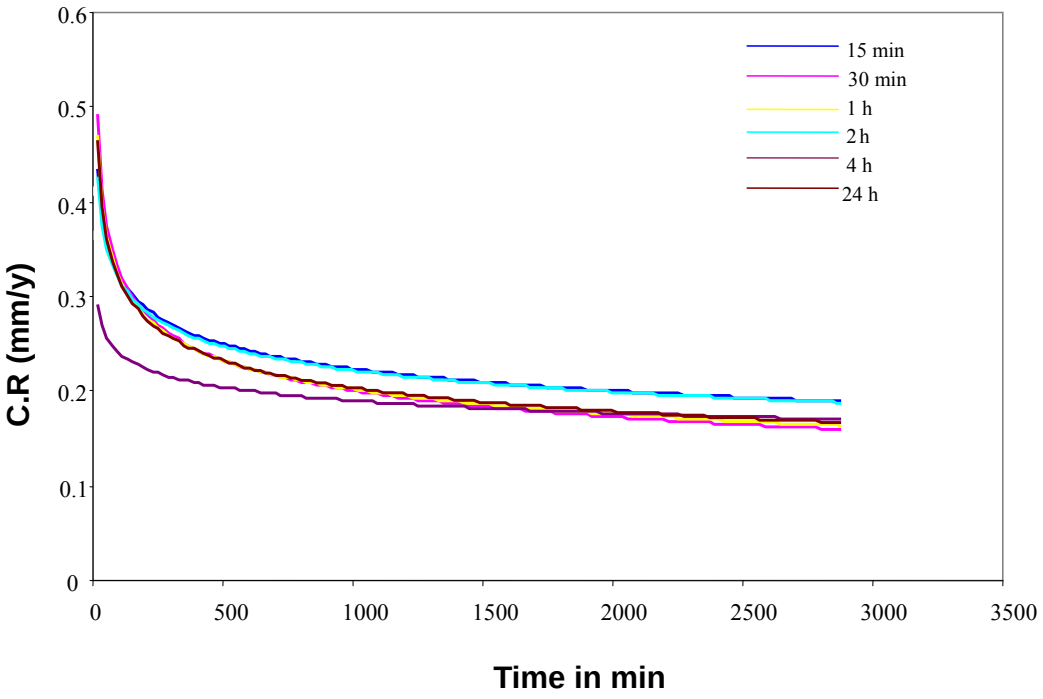

Figure 6. Corrosion rate values for layers formed by styrene-co-styphos acid on carbon steel.

Conclusions

1. Well ordered SAM layers were formed on different metal surfaces from phosphonic acids under investigation. The contact angle values were higher than 95° and in some cases it even reached 175° which indicated that these metal surfaces were almost not wetted by water, and could be considered as superhydrophobic ones.
2. The most hydrophobic layers that gave the highest contact angle values in water on all metals were formed from fluorophosphonic acid.
3. Layers formed from molecules with double bonds (undecenyl phosphonic acid), exposed to UV light showed a significant increase in the compactness on carbon steel because the polymerization improved the layer quality which was reflected in the higher contact angle values.
4. Concentration of the amphiphilic material's solution had an impact on the formation and quality of the layers. With increasing concentration the contact angles *i.e.*, the compactness of the layer increased.
5. Linear polarization measurements of the layers cured via UV illumination gave indication that film formed with undecenyl phosphonic acid at 24 h resulted in a low corrosion (0.05 mm/year).

6. Although layers formed by fluorophosphonic acid gave a low corrosion rate especially those formed at 4 h and 24 h, such results were not achieved by styrene-co-styphos acid where the corrosion rate values were high at all cases.

References

1. E. Jaehne, S. Oberoi and H.-J. P. Adler, *Progress in Organic Coatings*, 2008, **61**, 211.
2. Yu. I. Kuznetsov, *Bull. Electrochem.*, 1990, **6**, 571.
3. Yu. I. Kuznetsov, *Progress on the Understanding and Prevention of Corrosion, The Phosphonate Inhibitors for Metal Corrosion*, 1995, pp. 853–859.
4. Y. I. Kuznetsov, *Organic inhibitors of corrosion of metals*, ed. J. G. N. Thomas, Plenum Press, New York, London, 1996.
5. H. Amar, J. Benzakour, A. Derja, D. Villemin and B. Moreau, *J. Electroanal. Chem.*, 2003, **558**, 131.
6. A. Paszternák, S. Stichleutner, I. Felhősi, Z. Keresztes, F. Nagy, E. Kuzmann, A. Vértes, Z. Homonnay, G. Pető and E. Kálmán, *Electrochim. Acta*, 2007, **53**, 337.
7. M. Prabakaran, M. Venkatesh, S. Ramesh and V. Periasamy, *Appl. Surf. Sci.*, 2013, **276**, 592.
8. I. Felhősi and E. Kálmán, *Corros. Sci.*, 2005, **47**, 695.
9. T. Rigó, A. Mikó, J. Telegdi, M. Lakatos-Varsányi, A. Shaban and E. Kálmán, *Electrochem. Solid State Letters*, 2005, **8**, 51.
10. J. Telegdi, T. Rigó, J. Beczner and E. Kálmán, *Surf. Eng.*, 2005, **21**, 107.
11. A. Raman, R. Quiñones, L. Barriger, R. Eastman, A. Parsi and E. S. Gawalt, *Langmuir*, 2010, **26**, 1747.
12. E. Hoque, J. A. DeRose, B. Bhushan and K. W. Hipps, *Ultramicroscopy*, 2009, **109**, 1015.
13. E. Hoque, J. A. DeRose, P. Hoffmann and H. J. Mathieu, *Surf. Interface Anal.*, 2006, **38**, 62.
14. A. Alagta, I. Felhősi, I. Bertóti and E. Kálmán, *Corros. Sci.*, 2008, **50**, 1644.
15. C. N. C. Lam, R. Wu, D. Li and M. L. Hair, *Adv. in Colloid and Interface Sci.*, 2002, **96**, 169.

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